AFRL-RW-EG-TP-2015-001

Surface Impact Simulations of Helium Nanodroplets

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Grant No. FA8651-11-1-0005

June 2015

Distribution A: Approved for public release; distribution unlimited.
Approval Confirmation 96 TW-2015-0216 dated 30 June 2015

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REPORT DOCUMENTATION PAGE

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1. REPORT DATE *(DD-MM-YYYY)*
30-06-2015

2. REPORT TYPE
Technical Paper

3. DATES COVERED *(From - To)*
9 September 2011 – 8 December 2013

4. TITLE AND SUBTITLE
Surface Impact Simulations of Helium Nanodroplets

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA8651-11-1-0005

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Robert J. Hinde

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
W0QE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
University of Tennessee
Knoxville, TN 37996

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-RW-EG-TP-2015-001

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory, Munitions Directorate
Ordnance Division
Energetic Materials Branch (AFRL/RWME)
Eglin AFB FL 32542-5910
Technical Advisor: C. Michael Lindsay, PhD

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL-RW-EG

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RW-EG-TP-2015-001

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution unlimited. Approval Confirmation 96 TW-2015-0216, dated 30 June 2015

13. SUPPLEMENTARY NOTES
DISTRIBUTION STATEMENT INDICATING AUTHORIZED ACCESS IS ON THE COVER PAGE AND BLOCK 12 OF THIS FORM.
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14. ABSTRACT

We summarize here progress made on a two-pronged program of research, supported by AFRL, that uses theoretical and computational methods to investigate both (1) the formation of small metal atom aggregates inside the nanodroplets and (2) the desolvation and isolation of these aggregates through gentle surface impacts, or "soft landings". The first effort developed a highly parallel code suite, QDROP, that simulates the structure of neat and atom-doped He droplets using variational path integral (VPI) quantum Monte Carlo methods. We have used QDROP to study He droplets with as many as N = 1000 atoms of aluminum and magnesium doped systems. The second effort developed a framework for modeling droplet-surface impacts using a "dressed classical dynamics" code for simulating the real-time dynamics. These simulations are a modified version of zero-point averaged dynamics, which captures atomic delocalization of the helium atoms characteristic of the quantum solvent, but allow the single-particle wavefunctions to vary throughout the simulation, thereby allowing the densities to redistribute to their local environment.

15. SUBJECT TERMS
Helium Droplets, Soft landing, deposition, nanoclusters, molecular dynamics, QDROP, variational path integral, quantum Monte Carlo

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Michael Lindsay
a. REPORT UNCLASSIFIED	**b. ABSTRACT** UNCLASSIFIED	**c. THIS PAGE** UNCLASSIFIED	SAR	17	**19b. TELEPHONE NUMBER** *(include area code)* 850-882-1543

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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Surface impact simulations of helium nanodroplets

Final performance report: AFRL/RWK grant FA8651-11-1-0005

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1. Introduction

When a helium (He) nanodroplet passes through a pick-up chamber that contains a low-density atomic or molecular gas, the atoms or molecules that impinge upon the droplet's surface frequently stick to the droplet and migrate into the droplet's interior. If several of these dopant species dissolve in a single nanodroplet, they may coalesce inside the droplet and form a polyatomic aggregate. The low temperature ($T \approx 0.37$ K) inside He droplets can stabilize these aggregates in relatively high-energy structures that represent local, but not global, minima on the aggregate's potential energy surface. Helium droplets could thus potentially find applications as nanoscale, cryogenic "reaction chambers" for the preparation of exotic molecular species that have unusual chemical properties. Such an approach could be used in the near future to create, in an atom-by-atom fashion, nanostructured materials that serve as next-generation catalysts, propellants, or munitions.

For synthetic chemists to fully realize this potential, they must devise methods for removing the solvated aggregates from the He droplet in a nondestructive manner. One simple approach for doing this might be to gently "land" the doped He droplet on a solid surface; the hope here is both that the droplet's bulk would cushion the impact of the dopant aggregate with the underlying surface and that the droplet would fragment upon impact, with individual He atoms or small He_n clusters carrying away the center-of-mass kinetic energy of the doped droplet.

We summarize here progress made on a two-pronged program of research, supported by AFRL, that uses theoretical and computational methods to investigate both (1) the formation of small metal atom aggregates inside He nanodroplets and (2) the desolvation and isolation of these aggregates through gentle surface impacts, or "soft landings".

The first prong of work focused on the development of a highly parallel code suite, QDROP, that simulates the structure of neat and atom-doped He droplets using variational path integral (VPI) quantum Monte Carlo methods. We have used QDROP to study He droplets with as many as $N = 1000$ atoms; we believe these are the largest droplets studied to date using the VPI quantum Monte Carlo approach. Our results provide the first detailed atomistic picture of the dense solvation shells that surround atomic impurities solvated in He droplets; it has been speculated that if two Mg atoms or two Al atoms dissolve in a single He nanodroplet, these dense shells may impede recomination of the two metal atoms.

The second prong of work took initial steps toward developing a "dressed classical dynamics" code for simulating the real-time dynamics of neat and doped He droplets. In this approach, individual He atoms are treated as classical particles that are "dressed" with a single-particle wavefunction that represents each atom's delocalization in the droplet. Two He atoms in the simulation interact via a potential energy function that is obtained by averaging the bare He–He interaction over the two atoms' probability density distributions.

2. Summary of work completed

2.1 Quantum Monte Carlo studies of doped helium droplets

Mg-doped and Al-doped He nanodroplets have recently been investigated in several experimental laboratories [1–3]. These nanodroplets are prepared in pick-up experiments, in which large He droplets pass through a pick-up cell that contains a low pressure of Mg or Al vapor; by adjusting the metal atom vapor pressure, the typical number of metal atoms picked up by the droplet can be controlled. The experiments suggest that when a single droplet captures several Mg atoms or several Al atoms, the captured atoms do not form a strongly bound metal cluster inside the droplet. Instead, the metal atoms appear to form a weakly-bound "atomic foam" in which individual dopant atoms remain well separated from one another [1, 3].

Computational studies of metal-doped He droplets, based on helium density functional theory (He-DFT) treatments of the droplet, suggest that the first solvation shell of He atoms surrounding a metal atom dopant is likely to have a density substantially higher than that of bulk liquid helium [4, 5]. For Mg dopant atoms, as an example, the atomic density of the first solvation shell is predicted by He-DFT studies to be as high as 35 atoms/nm^3, or about 60% higher than the density of bulk liquid helium [4]. (This density is equivalent to the density of solid helium at a pressure of about 130 atm [6].) Interactions between the dense solvation shells that surround the individual dopant atoms are thus thought to play a key role in stabilizing the hypothesized "atomic foam" against recombination of the metal dopants.

A detailed investigation of the phenomena that contribute to the stability (or metastability) of these foams could not only help researchers understand the foams' unique properties, but could also shed light on the physics that governs the initial stages of metal aggregate formation in He nanodroplets. This could in turn help experimental scientists design protocols for using He droplets to synthesize metal atom aggregates with well-defined compositions and structures. Four recent reports [7–10] of metal cluster formation in He nanodroplets demonstrate the versatility and power of nanodroplet-assisted cluster synthesis.

We have developed a parallel code suite (powered by the Message Passing Interface parallel computing protocol) for the study of the structure of neat and doped He droplets using the variational path integral (VPI) quantum Monte Carlo (QMC) method [12, 13]. The code suite, QDROP, permits fully atomistic simulations of these systems that will complement the continuum He-DFT studies cited above. Specifically, the VPI QMC approach mitigates three shortcomings of the He-DFT studies:

(1) The He-DFT simulations are based on a helium density functional that is calibrated to the properties of bulk superfluid liquid helium. As we noted earlier, however, the solvation shells around metal atoms in He nanodroplets can have densities that are characteristic of solid helium under moderate pressure, and it is uncertain whether the helium density functionals typically used in He-DFT studies of metal-doped He droplets are reliable at these higher helium densities.

(2) The He-DFT studies treat the metal atoms as infinitely massive, immobile impurities. A fully atomistic approach that treats the helium atoms and metal dopants on an equal footing can help us understand whether dopant atom zero-point motions play an important role in the formation of the hypothesized atomic foams. Earlier theoretical studies suggest that dopants solvated inside He droplets undergo large-amplitude zero-point excursions away from the droplet center [11], and an accurate treatment of these large-amplitude excursions could be important in a quantitative investigation of weakly-bound dopant aggregates inside He droplets. By artificially increasing the dopant atom mass in our simulations, we can computationally suppress dopant zero-point motion; this will allow us to investigate the role that dopant zero-point motion plays in the solvation process.

(3) A fully-atomistic treatment allows us to incorporate three-body interactions into the underlying potential energy surface that describes the doped He droplet. At the elevated helium densities that characterize dopant solvation shells in He droplets, it may be important to include three-body forces if we are to treat the solvation shells quantitatively. Because the helium density functionals typically used to study dopant solvation in He droplets are calibrated to the properties of bulk superfluid liquid helium, any three-body interactions that are implicitly included in the parameterization of the functional represent an “average” three-body interaction characteristic of the liquid. Three-body interactions could be more significant at the higher densities found in dopant solvation shells.

VPI QMC simulations employ imaginary-time propagation techniques to obtain information about the quantum mechanical ground state of a many-body system. Operationally, the simulations map a quantum mechanical N-atom system onto a classical polymer of P “beads”; each bead represents a configuration of the underlying N-atom system and moves in a $3N$-dimensional coordinate space. Neighboring beads along the polymer chain are coupled by harmonic oscillator “bonds” that represent the portion of the imaginary-time propagator that is associated with the quantum mechanical kinetic energy operator. As $P \to \infty$, the polymer's two end beads attain asymptotic probability distribution functions that are equivalent to the N-atom system's ground state wavefunction, while the polymer's interior beads attain asymptotic probability distributions that are equivalent to the N-atom system's ground state probability distribution. VPI QMC simulations can therefore simultaneously provide both the ground state energy of the N-atom system and information about the expectation values of coordinate-space observables (such as pair correlation functions or one-body densities). VPI QMC simulations can readily be carried out on parallel computing platforms, and exhibit nearly linear speedup with the number of processors devoted to the simulation [14–17].

In Fig. 1 we show representative density profiles, computed using our QDROP code, for Ne-doped He droplets with $N = 75$ to 600 atoms. This figure shows the evolution, with increasing N, of the solvation shells that surround the Ne dopant. The first solvation shell is already present even at $N = 75$, but does not reach its asymptotic density of roughly 2.3 times the density of bulk liquid He until the droplet has $N = 600$ atoms. The second and third solvation shells can be easily recognized in the larger droplets; a fourth solvation shell is just beginning to emerge at $N = 600$.

At present, QDROP's execution time scales quadratically with the number of atoms in the He droplet. A ten-fold increase in the number of atoms in the droplet thus requires a 100-fold increase in the computational resources devoted to the problem. By using linked cell lists [20] to exclude distant atom–atom pairs from the computation of the total potential energy of the droplet, we can improve QDROP's scaling to be nearly linear with the number of atoms in the droplet. This will allow us to carry out VPI QMC studies of droplets with $N \approx 5000$ atoms using roughly $O(10^3)$ nodes of a massively parallel computing system and about one week of wall clock time. Droplets of this size are comparable to those employed in experimental pick-up experiments [21].

2.2 Molecular dynamics simulations of droplet soft landings

Classical molecular dynamics simulations are a mature computational workhorse for studying real-time chemical dynamics in large systems (with more than a dozen or so atoms). The molecular dynamics approach has recently been applied to study the desolvation of species embedded in nanodroplets by colliding the droplet with a solid surface [22]. In these simulations, droplets containing as many as 6000 particles (typically water molecules or argon atoms) are studied for periods of time as long as 300 picoseconds. This demonstrates that a molecular dynamics study of the soft landing of doped He nanodroplets containing as many as 5000 atoms could be technically feasible.

The main drawback to using classical molecular dynamics methods to simulate real-time dynamics of He nanodroplets is that these methods ignore both the substantial quantum mechanical delocalization of the individual helium atoms in the droplet and the quantum statistical effects that accompany the interchange of identical particles in a many-body quantum system. While including quantum statistics in a real-time simulation of 5000 identical atoms is nearly intractable at the moment, there are a variety of strategies for including the delocalized nature of individual atoms in a real-time classical dynamical simuulation of moderately quantum systems like liquid H_2 or liquid helium. One of these is zero-point averaged dynamics (ZPAD), which incorporates the effects of atomic delocalization by treating individual atoms as smeared-out probability distributions that move along classical trajectories. ZPAD simulations have recently been used, for example, to carry out 30-ps molecular dynamics simulations of doped He_N droplets with $N \approx 100$ [22–24].

ZPAD simulations treat individual He atoms in a droplet as frozen, spherically-symmetric probability density distributions $|\psi(\mathbf{r})|^2$, obtained as the square of a single-particle He atom wavefunction $\psi(\mathbf{r})$. The single-particle wavefunction is obtained through an iterative procedure that involves solving the three-dimensional Schrödinger equation for an individual He atom moving under the influence of its neighbors. The ZPAD method traces its genesis back to Einstein models [25–28] for the zero-point motions of atoms and molecules in low temperature, highly quantum Boltzmann solids.

One computational advantage of the ZPAD approach is that, because the single-atom probability density distributions $|\psi(\mathbf{r})|^2$ are computed "once and for all" at the beginning of the simulation, the underlying interatomic interactions that govern the droplets' impact dynamics can be pre-averaged over these probability density distributions to give effective interatomic potential energy curves that have zero-point averaging effects built into them [25]. This makes ZPAD simulations no more expensive than conventional classical molecular dynamics simulations.

However, one drawback of the ZPAD approach is that because the He atoms' probability density distributions are defined at the beginning of a simulation, these distributions cannot respond to changes in the atoms' local environment that occur during a simulation. As a He droplet makes a soft landing on a solid surface, we might expect the probability distributions of He atoms near the surface to temporarily acquire some degree of anisotropic character, as shown in Fig. 2. We are developing a classical dynamics method that extends the ZPAD method to incorporate these effects in simulations of He nanodroplets; here, we summarize our first steps in this project.

In the approach we propose, we will allow the He atoms' single-particle wavefunctions to vary during the simulation. Let $\psi_k(\mathbf{r}_k, t)$ represent the single-particle wavefunction for He atom number k at time t. We will expand this function in terms of a basis set of s localized functions $\{\phi_p(\mathbf{u}) : p = 1, 2, \ldots, s\}$ centered on the He atom's current average position $\langle \mathbf{r}_k \rangle$:

$$\psi_k(\mathbf{r}_k, t) = \sum_{p=1}^{s} c_{p,k}(t) \phi_p(\mathbf{r}_k - \langle \mathbf{r}_k \rangle) \ . \tag{1}$$

We then recompute, at each step along the molecular dynamics trajectory, the expansion coefficients $\{c_{p,k} : p = 1, 2, \ldots, s\}$ for atom k. This is akin to ab initio molecular dynamics (AIMD) approaches that carry out "on the fly" molecular dynamics simulations by re-computing electronic wavefunctions at each step along the molecular dynamics trajectory;

here, the He atom single-particle wavefunctions are the analogues of the electronic degrees of freedom in AIMD simulations.

By requiring the He atoms' single-particle wavefunctions to be constructed as linear combinations of the basis set functions $\{\phi_p(\mathbf{u}) : p = 1, 2, \ldots, s\}$, we can provide the atoms with flexibility to change their wavefunctions as the molecular dynamics trajecory evolves, but still retain most of the efficiency of the conventional ZPAD approach in evaluating zero-point averaged He–He interactions. If $V(r)$ is the bare He–He interatomic interaction, then the zero-point averaged interaction for He atoms j and k is given by

$$\langle \psi_j(\mathbf{r}_j)^2 \psi_k(\mathbf{r}_k)^2 V(|\mathbf{r}_k - \mathbf{r}_j|) \rangle \tag{2}$$

where the angle brackets represent averaging over the two atoms' zero-point probability distribution functions. Inserting the definition of $\psi_k(\mathbf{r}_k)$ from above, and letting $\mathbf{u}_k = \mathbf{r}_k - \langle \mathbf{r}_k \rangle$, we obtain

$$\sum_{p=1}^{s} \sum_{p'=1}^{s} \sum_{q=1}^{s} \sum_{q'=1}^{s} c_{p,j} c_{p',j} c_{q,k} c_{q',k} \langle \phi_p(\mathbf{u}_j) \phi_{p'}(\mathbf{u}_j) \phi_q(\mathbf{u}_k) \phi_{q'}(\mathbf{u}_k) V(\mathbf{R}) \rangle \tag{3}$$

where $\mathbf{R} = \mathbf{u}_k - \mathbf{u}_j + \mathbf{S}$ and $\mathbf{S} = \langle \mathbf{r}_k \rangle - \langle \mathbf{r}_j \rangle$ is the vector that connects the current mean positions of atoms j and k. The angle brackets in Eq. (3) represent averaging over the two three-dimensional vectors $\mathbf{u}_j$ and $\mathbf{u}_k$; the quantity in angle brackets is therefore a function only of the vector $\mathbf{S}$.

Because the basis set functions $\phi_p(\mathbf{u})$ have functional forms that do not change during the simulation, the averaging process represented in Eq. (3) can be carried out at a set of discrete $\mathbf{S}$ vectors, arranged on a large, dense three-dimensional grid, at the start of the simulation. On-the-fly computation of the interaction between He atoms j and k can then be done by interpolating these pre-averaged functions on the $\mathbf{S}$ grid, and combining the pre-averaged functions with the weighting coefficients as indicated by the summation in Eq. (3).

Our initial choice for the basis set functions $\phi_p(\mathbf{u})$ will be a set of low-lying three-dimensional harmonic oscillator functions. Our approach for choosing the force constant for the oscillator is described in more detail below. At each step of the simulation, the coefficients $\{c_{p,j}\}$ that define the zero-point motion for He atom j will be adjusted to minimize the He atom's zero-point energy in the field generated by nearby atoms. Using a set of harmonic oscillator functions thus provides the He atom with flexibility to adjust its own local wavefunction as the trajectory evolves.

We plan to use our modified ZPAD approach to simulate soft landings of doped He nanodroplets, containing $O(10^3)$ He atoms, in which the dopant is either an individual Mg atom or the weakly-bound Mg_2 dimer. We will study soft landings at surface impact velocities that are chosen in consultation with AFRL personnel to mimic realistic experimental conditions. For Mg_2 dopants, we will look for signs of Mg_2 dissociation as the doped droplet hits the surface. The primary goal of these simulations will be to understand what droplet sizes and impact velocities might lead to landings that are soft enough to minimize energy transfer from the droplet to the Mg_2 dopant, and that therefore allow the Mg_2 dopant to arrive at the surface intact and without substantial vibrational excitation. For simplicity, we will ignore the atomic structure of the landing surface and treat it as a smooth, impenetrable wall with a weak van der Waals physisorption well for the Mg or Mg_2 dopant. We will approximate the droplet's potential energy as the sum of pairwise additive He–He, He–Mg, and Mg–Mg interactions; these are averaged over the He atoms' zero-point motions as indicated in Eq. (3) to yield effective interatomic interactions at each step of the molecular dynamics trajectory.

We also plan to use our modified ZPAD approach to simulate the pick-up of Mg dopants by He nanodroplets. We will first simulate the pick-up of a single Mg atom by a droplet to understand the dynamical processes that dissipate (e.g. through He atom boil-off) both the relative kinetic energy of the atom–droplet pair and the solvation energy released when the atom dissolves in the droplet. We will then simulate the pick-up of a second Mg atom by a droplet already doped with a single Mg atom; these simulations will complement the VPI QMC studies described above by helping us understand whether Mg atoms can effectively surmount any recombination barrier that arises from their dense He solvation shells.

The force constant that defines the harmonic oscillator basis set for a given He atom will be obtained through a ZPAD-like approach. To test this approach, we have applied it to an ensemble of configurations that represent fragments of distorted hcp-like solid He crystals. Specifically, we take a 13-atom fragment, consisting of a central atom and its 12 nearest neighbors in the hcp crystal lattice. We scale the nearest-neighbor distance of the 13-atom fragment so that the fragment represents a configuration drawn from a lattice with a particular density. We then randomly jiggle the three Cartesian coordinates of each atom by adding a random displacement of up to ±10% of the nearest-neighbor distance.

Equipped with this distorted hcp-like lattice fragment, we then assume that each atom in the fragment is represented by a three-dimensional isotropic harmonic oscillator single-particle wavefunction. We adjust the force constant of these wavefunctions (keeping the force constant for all 13 He atoms the same) to minimize the total (kinetic plus potential) energy of the central He atom. Once we have minimized this energy, we then record the mean squared displacement $\langle u^2 \rangle$ of the central He atom; this contains the same information as the force constant, but is physically more meaningful.

Figure 3 shows the distribution of $\langle u^2 \rangle$ values for 1000 distorted hcp-like cages at three different target densities: 22.6 nm^{-3}, 27.8 nm^{-3}, and 34.8 nm^{-3}. These densities are respectively 3%, 28%, and 59% higher than the density of bulk liquid He, and have been chosen to span a range of densities that might be present in local regions of metal-doped He droplets.

We see from Fig. 3 that at each nominal density, the range of force constants (or mean squared displacement values) derived using this procedure spans a relatively narrow range, and appears to be represented by a roughly Gaussian probability distribution. This suggests that, for our modified ZPAD approach, the force constants that are associated with the harmonic oscillator basis set used to represent the He atoms' single-particle wavefunction can be quickly and accurately estimated from the local He atom density associated with each atom's immediate environment. (This local density can in turn be estimated from a Voronoi tesselation of the three-dimensional space in which the He atoms move.) Because of the relatively narrow range of force constants associated with a given nominal local He density, it appears that our modified ZPAD dynamics will be relatively insensitive to the exact value of the force constant chosen for each He atom in the droplet; however, this hypothesis remains to be tested through additional numerical experiments.

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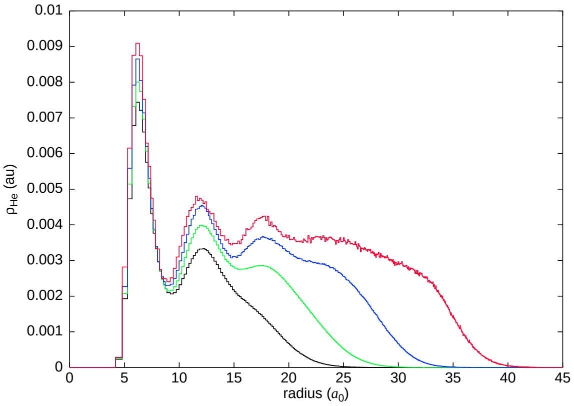

Fig. 1: Evolution of the solvation structure in Ne-doped He_N nanodroplets as a function of N. From left to right, the density profiles shown are for $N = 75$, 150, 300, and 600 He atoms. The Ne atom is held fixed at the center of the droplet.

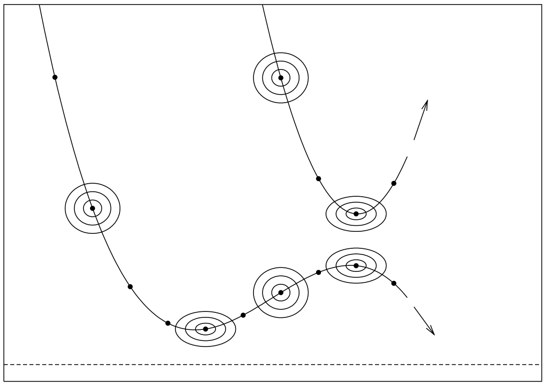

Fig. 2: A schematic depiction of two He atoms' trajectories in a molecular dynamics simulation. Both atoms carry single-particle wavefunctions along their trajectories, represented by the "bulls-eye" contour plots at selected points along the trajectory. One atom collides with a repulsive wall (at the bottom of the figure) and then with a second atom. Note the slight deformation of the single-particle wavefunctions during the collisions.

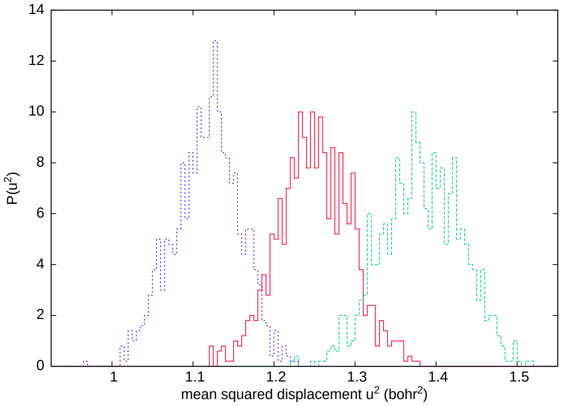

Fig. 3: Probability distributions for the mean squared displacement $\langle u^2 \rangle$ for He atoms in distorted hcp-like cages. The ensemble of distorted cages is generated following a procedure described in the text. The nominal densities of the systems are, from left to right: 34.8 nm^{-3} (blue), 27.8 nm^{-3} (red), and 22.6 nm^{-3} (green).

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